

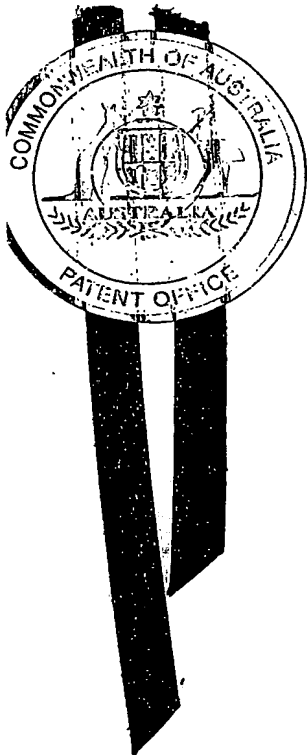


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**PATENTS ACT 1990**

**PROVISIONAL SPECIFICATION**

for the invention entitled:

**"METAL ALLOYING PROCESS"**

The invention is described in the following statement:

## METAL ALLOYING PROCESS

### Background and Prior Art

- 5 This invention concerns the addition of materials to molten metals. It has particular applicability to the addition of alloying elements to light metals and more particularly to the addition of zirconium to magnesium or magnesium alloys.

10 Zirconium is a potent grain refiner for magnesium alloys that contain negligible Al, Mn, Si, Fe, Ni, Co, Sn and Sb (zirconium forms stable compounds with these elements) [1]. When added to these magnesium alloys in a proper quantity (normally around 1%), zirconium can readily cause the grain size to decrease by 80% or more under normal cooling rates. In addition, the unfavourable iron content can be readily brought down to under 0.005% from a normal level of 0.02-0.04% [2]. The  
15 exceptional grain refining ability makes zirconium an important alloying element for magnesium alloys that are not based on alloying with Al and Si. For example, zirconium containing Mg-RE-Zn alloys such as EZ33 (Mg-3.3RE-2.7Zn-0.6Zr) and ZE41 (Mg-1.2RE-4.2Zn-0.7Zr) offer a specific combination of elevated temperature and room temperature properties not achievable with the Mg-Al-Zn alloys [3].

20 The solubility of Zr in molten pure Mg is approximately 0.6% [3], which slightly increases with increasing melt temperature. The most characteristic feature of the microstructure of a magnesium alloy that contains more than a few tenths per cent soluble zirconium is the zirconium-rich cores that exist in most of the magnesium  
25 grains [4]. These zirconium-rich cores are believed to be the products of peritectic solidification [4]. In order to achieve excellent grain refinement in commercial production, it is desirable to dissolve the full zirconium content (i.e., 0.6%) in a magnesium melt [4].

- 30 To date, various approaches have been explored to introduce zirconium into molten magnesium. These include [1, 6]:
- (a) alloying with different forms of zirconium metal,

- (b) alloying with zirconium sponge,
- (c) alloying with Zn-Zr master alloys,
- (d) alloying with  $ZrO_2$ ,
- (e) alloying with various zirconium halides or complex halides or a mixture of
- 5 halides and/or complex halides with different salts such as NaCl, KCl,  $BaCl_2$ ,  
NaF, KF, etc, and
- (f) alloying with Mg-Zr master alloys.

The advantages and disadvantages of each of these processes have been discussed in  
10 detail by Saunders and Strieter [6] and Emley [1]. For commercial manufacture, there  
have been only two types of zirconium alloying material in widespread use since 1960  
[1]. These are zirconium-rich Mg-Zr master alloys based on the fluoride and chloride  
salt reduction processes. Both types of master alloy are essentially the same and  
contain about one third their weight of zirconium [1]. One of them, developed by  
15 Magnesium Elektron Ltd. (MEL) via chemical reduction of zirconium fluoride with  
molten magnesium, has been long known as Zirmax (trade mark). This development  
was first made by MEL as far back as 1945 [1]. The similar type of Mg-Zr master  
alloy developed in the United States approximately during the same period was based  
on a chloride salt reduction process [6]. But it was not until about 1960 that MEL  
20 replaced its salt reduction alloying processes by Zirmax. Before that (from 1947 to  
1959), master salt was used for virtually all magnesium-zirconium alloy production in  
the U. K. and other European countries, and to a gradually increasing extent in the  
USA [1].

25 At present the Zirmax type master alloy is still the primary zirconium alloying  
material used for the commercial production of zirconium-containing magnesium  
alloys. It contains approximately 33% Zr and 67% Mg, in which most zirconium is  
present as various sizes of zirconium particles (mostly in the range of submicron to 10  
 $\mu m$ ) in a magnesium matrix [7].

30

The present invention particularly deals with the use of zirconium metal as a grain  
refiner for magnesium alloys and, in the following discussion of the prior art, special

emphasis will be given to the background of alloying zirconium metal to magnesium based on references 1 and 6.

Sauerwald [8] published his work on alloying zirconium metal powder to magnesium in 1947. He added 5 wt% zirconium metal powder to magnesium under an argon atmosphere at various temperatures between 680 and 1100°C. Soluble zirconium contents exceeding 0.5 wt% (samples were digested in HCl acids) were obtained at all temperatures tested. Ball [9] in the same year described the British work and stated that metallic zirconium dissolves in magnesium under an argon atmosphere at 900-1100 °C but it is a difficult and costly process. Emley [10] in 1948 pointed out that as the zirconium metal powder is expensive and highly inflammable, it is natural to consider the possibility of alloying by a reducible zirconium compound.

In 1952, Saunders and Strieter [6] published their work "Alloying Zirconium to Magnesium", in which different metallic forms of zirconium, i.e., zirconium sponge, fused zirconium, iodide-decomposed ductile zirconium, and zirconium powder, were investigated as zirconium alloying materials for magnesium at 760 °C (1400 F). The fused lump zirconium was added as 6.35-mm (¼-in.) pieces in a small steel ladle and stirred in the ladle with a steel rod. No apparent solution had occurred after 30 minutes of stirring. Analysis of the melt showed a result of 0.03% soluble zirconium content with 1% zirconium addition. Iodide zirconium sheet, rolled to about 127 – 254µm (0.005-0.010 in.) and cut into 6.35mm (¼-in.) squares was added in a manner similar to that used for the fused lump zirconium. It was stirred for several minutes in the ladle. It was found that after 65 minutes of holding at temperature, the resultant soluble zirconium content merely reached 0.1% with 1% zirconium addition. The use of zirconium powder was evaluated by adding it in different ways. This is because zirconium powder is pyrophoric and some means of protecting the powder from oxidation had to be applied. In the work referenced [6], materials tested were zirconium powder pelleted with various binders, zirconium powder enclosed in tight magnesium capsules, sintered zirconium powder briquettes, and zirconium powder compacted with magnesium powder. In general, with 3% zirconium addition to a Mg-5Zn melt, the resultant zirconium content varied between 0.7 and 0.85% as reported.

The solubility of zirconium in magnesium is influenced by the presence of a third element. It is reported that with the presence of Zn at a level around 3-4%, the solubility of Zr in magnesium could be increased from 0.6% to slightly over 0.7% and 5% zinc increases the solubility of Zr in magnesium to about 0.8% [6].

According to Saunders and Strieter [6], of the various metallic forms of zirconium tested, alloying with zirconium sponge demonstrated the most promising results. The zirconium sponge used was made by the Kroll process (sublimation of Mg and  $Mg_2Cl$  from the reaction product of  $Mg + ZrCl_4$ ) [6]. In their experiments, the sponge was essentially ground with the average size being reduced to about 12.7  $\mu m$  or 0.0005 in. The results showed that zirconium sponge produced a soluble zirconium content of about 0.62-0.66% in Mg-5Zn alloys with 3% zirconium addition after 3-4 minutes stirring. With 1% zirconium sponge addition, soluble zirconium contents in the range of 0.32 to 0.52% were achieved. Furthermore, the authors found that the alloying efficiency decreased when the sponge fragments were decreased in size because when the particles became finer powder, the material burned up before it could be submerged beneath the melt. Therefore, some means of protecting the powder from oxidation had to be applied.

20

Despite the excellent alloying results demonstrated by the work of Saunders and Strieter [6] with Kroll process zirconium sponge, alloying zirconium sponge to magnesium was in general limited to laboratory scales. As realised and pointed out by Saunders and Strieter [6], "an important disadvantage in the commercial use of sponge in the magnesium alloying field is the rather laborious effort required to alloy the material". This laborious effort apparently refers to the grinding process because the alloying process employed, i.e., 3-4 minutes of stirring, was plainly simple. In addition, the unavoidable contamination problem arising from the grinding process is another important disadvantage in the commercial use of zirconium sponge.

30

The remarks given by Emley [1] in his well-known *Principles of Magnesium Technology* about alloying zirconium metal to magnesium are: "pure zirconium metal

is expensive by any route and very inflammable in powder form, and for these reasons, coupled with the ease with which it becomes contaminated with oxygen, hydrogen and nitrogen, the approach via zirconium metal is not obviously the best".

- 5 Experiments have indicated that in commercial production of magnesium alloys, when Zirmax is dissolved into a magnesium melt at commercially useful addition rates, undissolved zirconium particles can be readily observed in the microstructure of the magnesium alloy produced [7, 11]. Many of these residual (undissolved) zirconium particles have an average size of around 5  $\mu\text{m}$ . It would be desirable if  
10 these zirconium particles could be smaller than those produced by using Zirmax so that more zirconium particles were available for nucleation of magnesium grains. Much improved grain refinement could be achieved by a denser nucleation.

The density of zirconium is  $6.5\text{gcm}^{-3}$  whereas the density of molten magnesium is  
15  $1.6\text{gcm}^{-3}$ . Therefore the zirconium particles have a strong tendency to settle in the melt unless stirred vigorously [7]. The larger the particle, the faster it settles out to the bottom of the melt. For example, a 15-micron zirconium particle falls at approximately 40 mm/min to the bottom of a magnesium melt at 780 °C and is therefore difficult for these particles to maintain suspended in the melt at this  
20 temperature [7]. By contrast, when the particle size is smaller than 3 microns, it can be readily suspended in the magnesium melt at the same temperature [7].

An aim of the present invention is to provide an improved alloying method, particularly a method of introducing zirconium metal to magnesium alloys. The  
25 present invention alleviates the difficulties highlighted above while excellent alloying results are produced.

#### References

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## 20 **Summary of the invention**

In one aspect the invention provides a method of adding an alloying element to a molten metal, comprising:

- (i) selecting a metallic sponge containing the alloying element,
- 25 (ii) washing the sponge in an acid solution, and
- (iii) submerging the sponge in said molten metal and stirring the molten metal.

The sponge may be rinsed and dried after the washing step. The sponge is preferably a porous agglomerate of metallic grains.

30

The invention is particularly applicable to the incorporation of zirconium into magnesium. So, in another aspect, the invention provides a method of adding



zirconium to molten magnesium, said method comprising:

- (i) selecting a metallic sponge containing zirconium,
- (ii) washing the sponge in an acid solution, and
- (iii) submerging the sponge in said molten magnesium and stirring the molten metal.

The acid solution may be HF at a concentration between 0.10% and 50.0%, preferably between 0.50% and 5.0% and more preferably between 1.5% and 2.5%, with the acid concentrations calculated as shown later in this specification. These acid concentration ranges correspond respectively to 0.05 – 50.0 molar, 0.25 – 2.63 molar and 0.76 – 1.28 molar, which may be rounded to 0.05 – 50, 0.25 – 3.0 and 0.75 – 1.5 molar.

Preferably the sponge comprises zirconium with only incidental impurities. Hafnium is a common impurity in zirconium. In contrast, Fe, Ni, Mn, Al, Si, C, Co, Sn and Sb are undesirable as they are alloying inhibiting and their total concentration is preferably less than 1% and more preferably less than 0.5%.

Preferably the amount of zirconium added to the molten magnesium is greater than that required to saturate the magnesium with zirconium at the temperature of the melt.

Preferably the zirconium sponge is in the physical form of small particles and each particle has a porous structure. Preferably these zirconium sponge particles have the following properties:

- the particles have an average size between 0.1 to 10 mm, more preferably between 0.5 and 5mm
- the particles have a minimum size of 0.5mm, more preferably 1mm, and a maximum size of 10mm, more preferably 5mm
- density of sponge =  $5.2\text{--}6.3\text{g/cm}^3$ , more preferably  $5.5\text{--}5.8\text{g/cm}^3$
- porosity of sponge  $(1 - (\text{density of sponge})/(\text{density of solid zirconium})) = 0.08\text{--}0.2$ , more preferably  $0.11\text{--}0.15$ .
- the void sizes on a polished transverse section of each zirconium sponge

particle are in general between 5 and 60  $\mu\text{m}$ .

In a further aspect the invention may provide a method of adding an alloying element to a molten metal, comprising:

- 5 (i) selecting a metallic sponge containing the alloying element,
- (ii) washing the sponge in a source of fluoride ions, and
- (iii) submerging the sponge in said molten metal and stirring the molten metal.

10 The sponge may be rinsed and dried after the washing step. The sponge is preferably a porous agglomerate of metallic grains.

In a further aspect, the invention may provide a method of adding zirconium to molten magnesium, said method comprising:

- 15 (i) selecting a metallic sponge containing zirconium,
- (ii) washing the sponge in a source of fluoride ions, and
- (iii) submerging the sponge in said molten magnesium and stirring the molten metal.

20 The source of fluoride ions may be an acidified solution containing fluoride ions or may be hydrofluoric acid at a concentration between 0.10% and 50.0%, preferably between 0.50% and 5.0% and more preferably between 1.5% and 2.5% when calculated as described elsewhere in this specification.

## 25 **Brief Description of the Figures**

In order that the invention may be more fully understood there will now be described, by way of example only, preferred embodiments and other elements of the invention with reference to the accompanying illustrations where:

30

Figures 1(a)-(c) are micrographs illustrating the grain refining ability of as-received and untreated sponge when added to pure magnesium at 730 °C. All

micrographs are of the same magnification. (a) Pure magnesium, (b) after adding 1% sponge, followed by 30 minutes manual stirring, and (c) adding a further 1% sponge and applying 30 minutes manual stirring.

5' Figures 2(a)-(c) are micrographs showing the grain refining ability of as-received and untreated sponge when added to pure magnesium at 780 °C. All micrographs are of the same magnification. (a) Pure magnesium, (b) after adding 1% sponge, followed by two minutes manual stirring and then 30 minutes holding, and (c) a further holding of 210 minutes at temperature.

10 Figures 3(a)-(c) show the grain refining ability of pretreated sponge when added to pure magnesium at 680 °C. All micrographs are of the same magnification. (a) Pure magnesium, (b) after adding 1 wt% sponge, followed by 20 minutes manual stirring, and (c) after a further 10 minutes stirring.

15 Figures 4(a)-(c) are optical micrographs showing the grain refining ability of pretreated sponge when added to pure magnesium at 730 °C. All micrographs are of the same magnification. (a) Pure magnesium, (b) after adding 1 wt% sponge, followed by 30 minutes manual stirring, and (c) after 30 minutes of holding following (b) and then restirring the melt for two minutes.

20 Figures 5(a)-(c) show the grain refining ability of pretreated sponge when added to pure magnesium at 800 °C. All micrographs are of the same magnification. (a) Pure magnesium, (b) after adding 1 wt% sponge, followed by 30 minutes manual stirring, and (c) after a further holding of 30 minutes and then restirring the melt for two minutes.

25 Figure 6 is a micrograph showing the physical form of zirconium sponge particles as used in one embodiment of the present invention.

30 Figure 7 is a micrograph showing a view of a typical microstructure of the zirconium sponge particles shown in Figure 6.

Figure 8 is a micrograph showing a view of an alternative microstructure for the zirconium sponge particles shown in Figure 6.

5           Figure 9 is a schematic diagram illustrating the method of adding zirconium sponge to molten magnesium.

10           Figure 10 is a backscattered electron (BSE) image of the grain structures of one of the samples taken from the 730 °C alloying test, showing the white tiny zirconium particles and the zirconium-rich cores, further demonstrating that the use of zirconium sponge is comparable to that of Zirmax.

15           Figure 11 is a backscattered electron (BSE) image of the grain structures of a sample prepared using Zirmax as per normal commercial production.

### 20           **Description of Examples of the Invention and the Preferred Embodiment**

The procedures followed are set out in the following steps numbered 1 to 5.

#### 20           **1. Comparison trials**

A zirconium sponge in the physical form of zirconium sponge particles of size 1-10 mm diameter was selected. The major impurity in the sponge was hafnium. The impurity concentrations were:

25           Hf = 0.8% approx

Fe+Cr = 0.1%

C = 0.004%

H = 0.001%

N = 0.002%

30           The sponge was added, without pretreatment, to two samples of molten magnesium at 730 and 780 °C respectively. Cone samples ( $\phi 30 \times \phi 20 \times 25$  mm) were collected at

different times and examination showed little evidence of grain refinement (Fig. 1 and Fig. 2) even when the melt was held at 780 °C for 2 to 6 hours. Wet chemical analyses of the soluble zirconium contents in the samples using 15% HCl acid showed negligible zirconium contents ( $< 0.05\%$ ).

5

## 2. The washing and cleaning process

Zirconium sponge identical to that used in the comparison trials above was first washed in an acid solution and was prepared in the following manner:

10 45ml concentrated nitric acid (68.5%-69.5%) and 45ml concentrated hydrofluoric acid (50%) were combined and diluted in water to a total of 1000ml. This gave an acid solution of approximately 3%  $\text{HNO}_3$  and 2% HF, which equates to approximately 1.1 molar HF and 0.5 molar  $\text{HNO}_3$ .

15 The zirconium sponge was left in this acid solution for 5 minutes. Bubbling was observed which indicated that the acid had probably at least partially removed the  $\text{ZrO}_2$  layer and was dissolving some of the zirconium metal underneath. The zirconium sponge was then rinsed in ethanol and dried.

20 An alternative washing process which was found satisfactory comprises washing the sponge in 0.25-0.5% HF. This is a very dilute HF acid solution and is readily handled. 0.5% HF was prepared by diluting 1ml concentrated Hydrofluoric acid (50%) to 100ml with water.

25 Concentrated nitric acid does not seem to work. Aqua regia works very slowly. The use of a heating plate slightly improves the washing process.

Although it is thought that successful washing involves the dissolution or some physical removal of oxide from the Zr surface, we do not wish to be bound by any  
30 theory as to why such a washing step is effective.

### 3. The drying process

The washed and rinsed zirconium sponge was dried under heating lamps at approximately 50°C for 60 minutes.

### 4. The addition process

A hole was machined into a small piece of magnesium ingot and the required pieces of zirconium sponge were placed into the hole as illustrated in Figure 9. This piece of ingot was then quickly submerged below the magnesium melt surface. This allowed the zirconium sponge to be introduced directly to the melt without the possibility of it remaining on the surface of the melt. It avoided oxidation of the Zr, avoided it being trapped into dross, and avoided the Zr not being wetted by the melt. The sponge could be added to the melt in other ways, such as by adding a compact of sponge particles, providing that it is successfully introduced below the surface.

It has been found that, alternatively, the zirconium sponge particles can be directly added to the melt under certain circumstances. An example is if the magnesium melt surface is protected with cover gas such as 1% SF<sub>6</sub> (balance: 49.5% CO<sub>2</sub> and 49.5% dry air), and the concentration of oxygen above the surface of the magnesium melt is therefore very low, the sponge particles can be successfully added directly providing it is done quickly. For example, the zirconium sponge particles can be added at a height of 800 mm away from the melt surface through a steel funnel, where the bottom of the funnel is placed just above the melt surface. This allows the sponge particles to quickly get into the melt without being oxidised. This has been proved to be a very convenient way of adding small (< 5mm) zirconium sponge particles to magnesium melts.

### 5. The Alloying Process

After addition of the zirconium sponge at a rate of 1% by weight, the melt was left for a couple of minutes to reheat to the correct temperature and was then stirred for 30

minutes. Three temperatures were used: 680, 730 and 800 °C. Cone samples were collected at different times after the addition of pretreated sponge.

Figures 3 to 5 show a typical view of the grain structures achieved from the three tests, respectively.

Zirconium sponge demonstrated a faster dissolution rate at 730 °C than at 680 °C. But in both cases, after 60 min. at temperature, the grain size obtained was around 80-90µm. It is believed that the grain size could be further reduced by increasing the holding time at 680 °C or intensifying the stirring operation or to apply both.

Figure 10 shows a BSE image of the grain structure of the sample shown in Figure 3(c). There are many tiny zirconium particles and many zirconium-rich cores in the microstructure. It looks very similar to the grain structure shown in Figure 11 obtained from using Zirmax.

Preliminary wet chemical analysis results indicate superior incorporation of zirconium than achieved if using Zirmax under the same conditions. These results are summarised in Table 1 which lists the wet chemical analysis results of soluble zirconium contents in samples taken from all three alloying tests.

Table 1 Soluble and total zirconium contents of samples by wet chemical analysis (%)

	Alloying temperatures					
	680°C		730°C		800°C	
	1 wt% sponge addition		1 wt% sponge addition		1 wt% sponge addition	
	Soluble*	Total**	Soluble	Total	Soluble	Total
	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
30 min. stirring	0.48	0.93	0.56	0.76	0.54	0.92
A further 30 min. holding			0.56	0.85	0.56	0.66

Restirring for 2 min.			0.56	0.97	0.57	0.74
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\* Soluble: 15% HCl    \*\* Total: 50% HCl + 6% HF

As can be seen, the soluble zirconium content reached 0.56% at both 730 and 800°C after 30 min. stirring. This is very close to the solubility limit of zirconium, i.e., 0.6 wt%, in molten pure magnesium. The soluble zirconium contents obtained with the same amount of zirconium addition in Zirmax master alloy are generally less than 0.5% for many tests conducted and are typically around 0.4% at 720°C [11]. The use of pretreated zirconium sponge showed a better recovery compared with the use of the Zirmax master alloy.

XPS analyses of treated and untreated sponge particles gave the results shown in the following table. For each analysis given, information was collected from a depth of 5 nanometers or 10 atomic layers on the surfaces of six different large particles.

15

Table 2 XPS analyses of treated and untreated sponge particles

Sponge Particles	Surface composition in atom percentage								
	C	O	Zr	Fe	Si	F	Cl	Mg	Hf
Untreated	30.5	49.2	16.2	1.1	3.0	0	0	0	0
Treated particles (black)	10.3	43.3	14.9	1.3	2.3	27.8	0	0	0
Treated particles (grey)	26.0	41.1	15.6	1.1	1.7	27.4	0	0	0

According to the energy level detected for each element, it is confirmed that O is present in the form of  $ZrO_2$  in all three cases studied and the detected F in the treated particles is present in the form of  $ZrF_4$  in all three cases studied.

20

The extra O ( $Zr:O = 1:2$  in  $ZrO_2$ ) is most likely due to the presence of oxidised C, Fe and Si on the surface.

For both treated and untreated particles, the surface is covered with a layer of  $ZrO_2$ .



The atom percentage of O does not change much after treatment.

Although we do not wish to be bound by any theory, it is presently thought that the mechanism is that there might be some defects or tiny voids existing on the surface or there are some "weak" sites on the  $\text{ZrO}_2$  and that these sites are attacked by the dilute HF solution. Consequently, tiny patches of  $\text{ZrF}_4$  would be formed on these attacked sites. Owing to the formation of such  $\text{ZrF}_4$  patches, oxidation of zirconium would be prevented on these sites after treatment. It is thought that the  $\text{ZrF}_4$  then dissolves into molten magnesium, leaving parts of the zirconium surface exposed to the zirconium even though most of it is still protected by a  $\text{ZrO}_2$  covering. When such treated particles are introduced into molten magnesium, the dissolution of different patches or  $\text{ZrF}_4$  on the particle surface would provide many fresh contact sites or channels with molten magnesium. This causes the dissolution of the whole sponge particle. Note that there are many tiny channels existing in each sponge particle as revealed by the BSE images. This would explain the disintegration of the sponge particles.

The above proposed mechanism is offered only as a possible explanation of the experimental results and there could be other mechanism(s). The present invention may incorporate but is not to be considered limited by the mechanism described.

20

Whilst the above description includes the preferred embodiments of the invention, it is to be understood that many variations, alterations, modifications and/or additions may be introduced into the constructions and arrangements of parts previously described without departing from the essential features or the spirit or ambit of the invention.

25

For example although the described preferred embodiment is directed to the introduction of zirconium into magnesium, other elements may also be introduced.

It will be also understood that where the word "comprise", and variations such as "comprises" and "comprising", are used in this specification, unless the context requires otherwise such use is intended to imply the inclusion of a stated feature or

30

features but is not to be taken as excluding the presence of other feature or features.

The reference to any prior art in this specification is not, and should not be taken as,  
an acknowledgment or any form of suggestion that such prior art forms part of the  
5 common general knowledge in Australia.

Dated this 18th day of January 2002

**CAST Centre Pty Ltd**

by their patent attorneys Morcom Pernat

**Fig. 1**

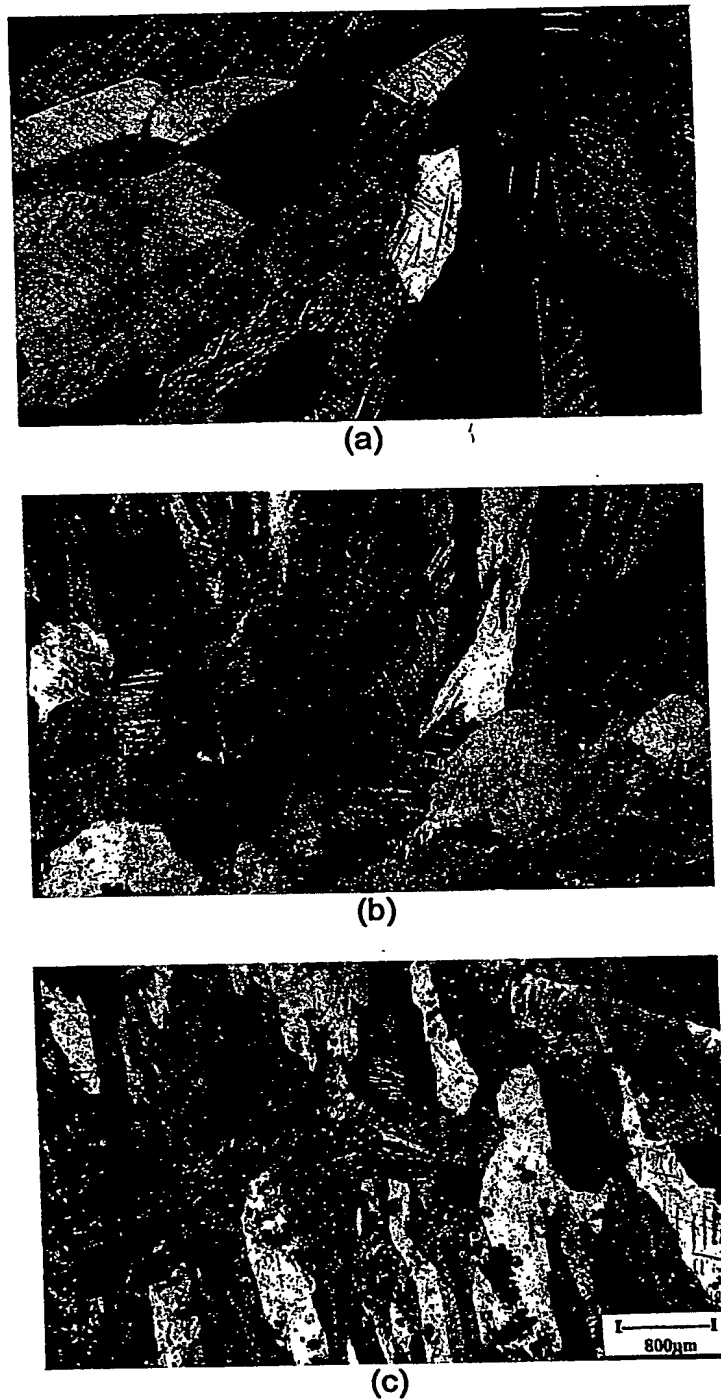


Figure 1 Optical micrographs showing the grain refining ability of as-received sponge when added to pure magnesium at 730 °C. All micrographs are of the same magnification. (a) Pure magnesium, (b) after adding 1% sponge, followed by 30 minutes manual stirring, and (c) adding a further 1% sponge and applying 30 minutes manual stirring.

**Fig. 2**

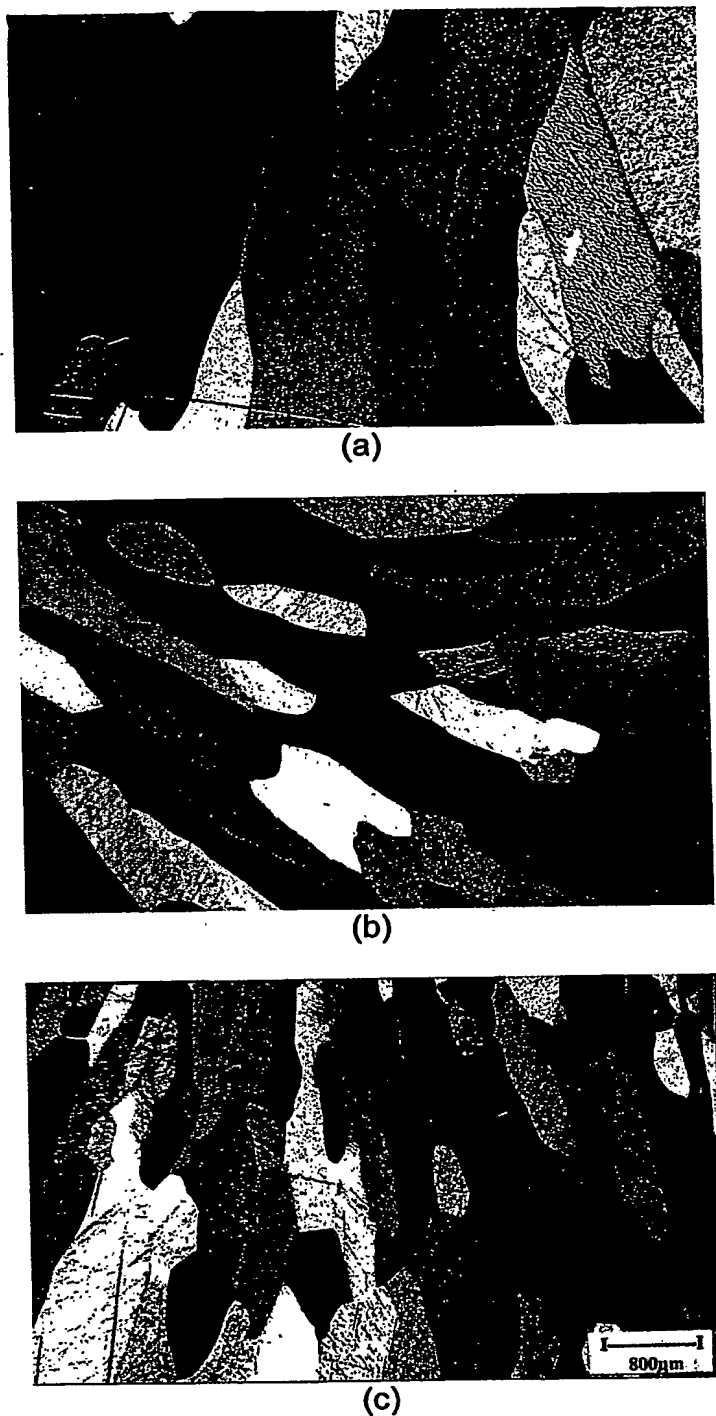


Figure 2 Optical micrographs showing the grain refining ability of as-received sponge when added to pure magnesium at 780 °C. All micrographs are of the same magnification. (a) Pure magnesium, (b) after adding 1% sponge, followed by two minutes manual stirring and then 30 minutes holding at temperature, and (c) a further holding of 210 minutes at temperature.

**Fig. 3**

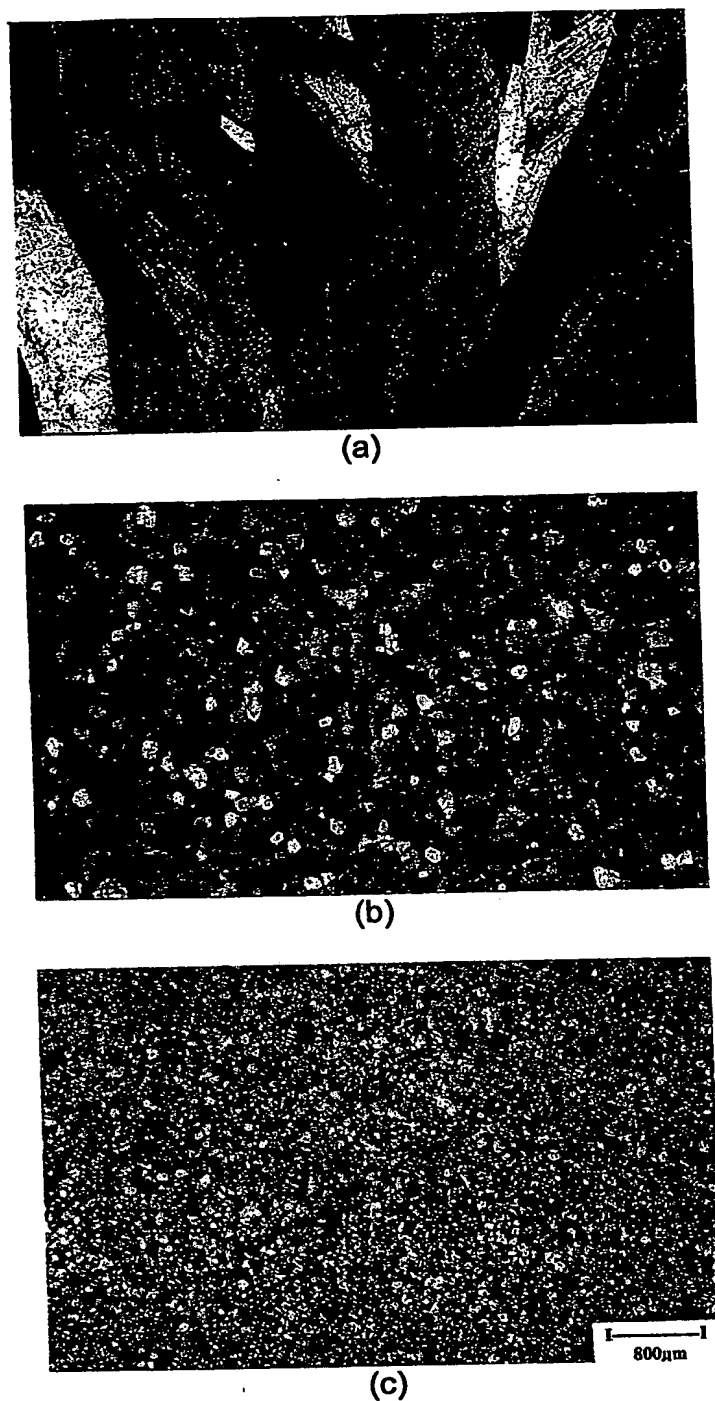


Figure 3 Optical micrographs showing the grain refining ability of pretreated sponge when added to pure magnesium at 680 °C. All micrographs are of the same magnification. (a) Pure magnesium, (b) after adding 1 wt% sponge, followed by 20 minutes manual stirring, and (c) after a further 10 minutes stirring.

**Fig. 4**

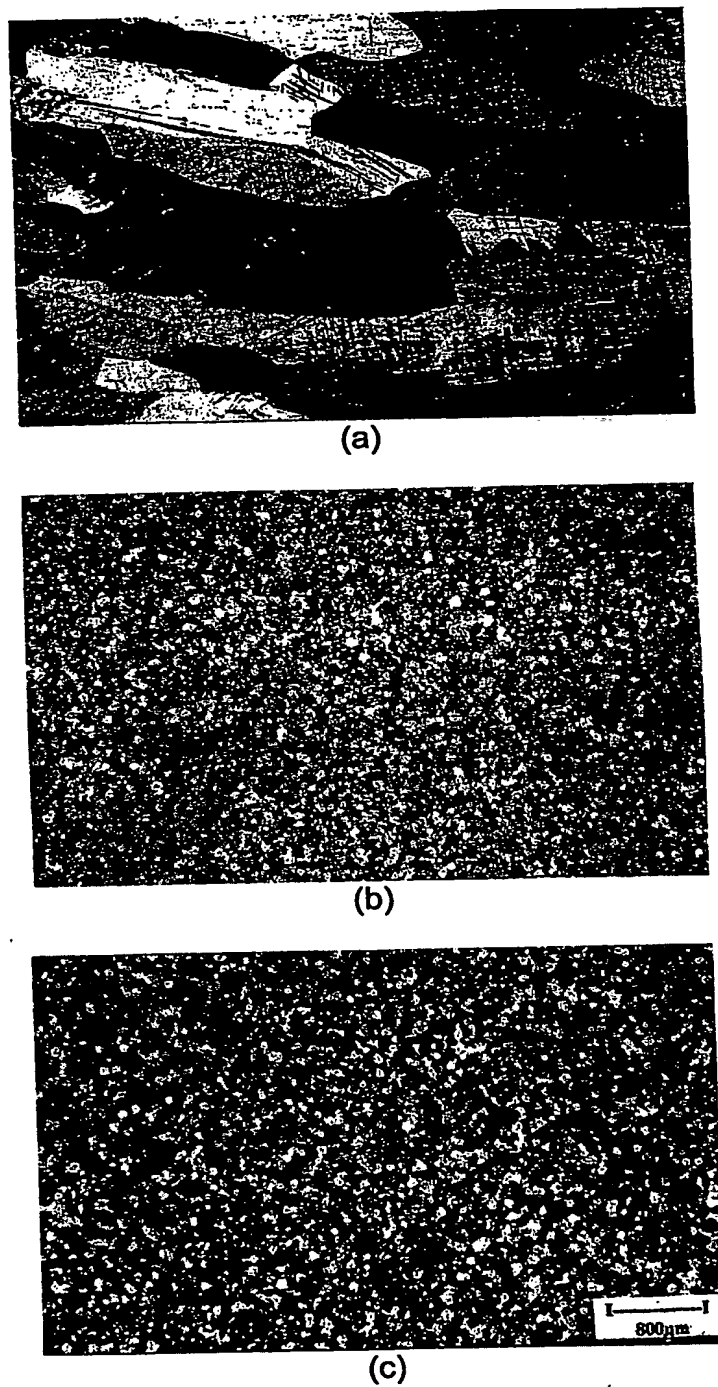


Figure 4 Optical micrographs showing the grain refining ability of pretreated sponge when added to pure magnesium at 730 °C. All micrographs are of the same magnification. (a) Pure magnesium, (b) after adding 1 wt% sponge, followed by 30 minutes manual stirring, and (c) after 30 minutes of holding following (b) and then restirring the melt for two minutes.

**Fig. 5**

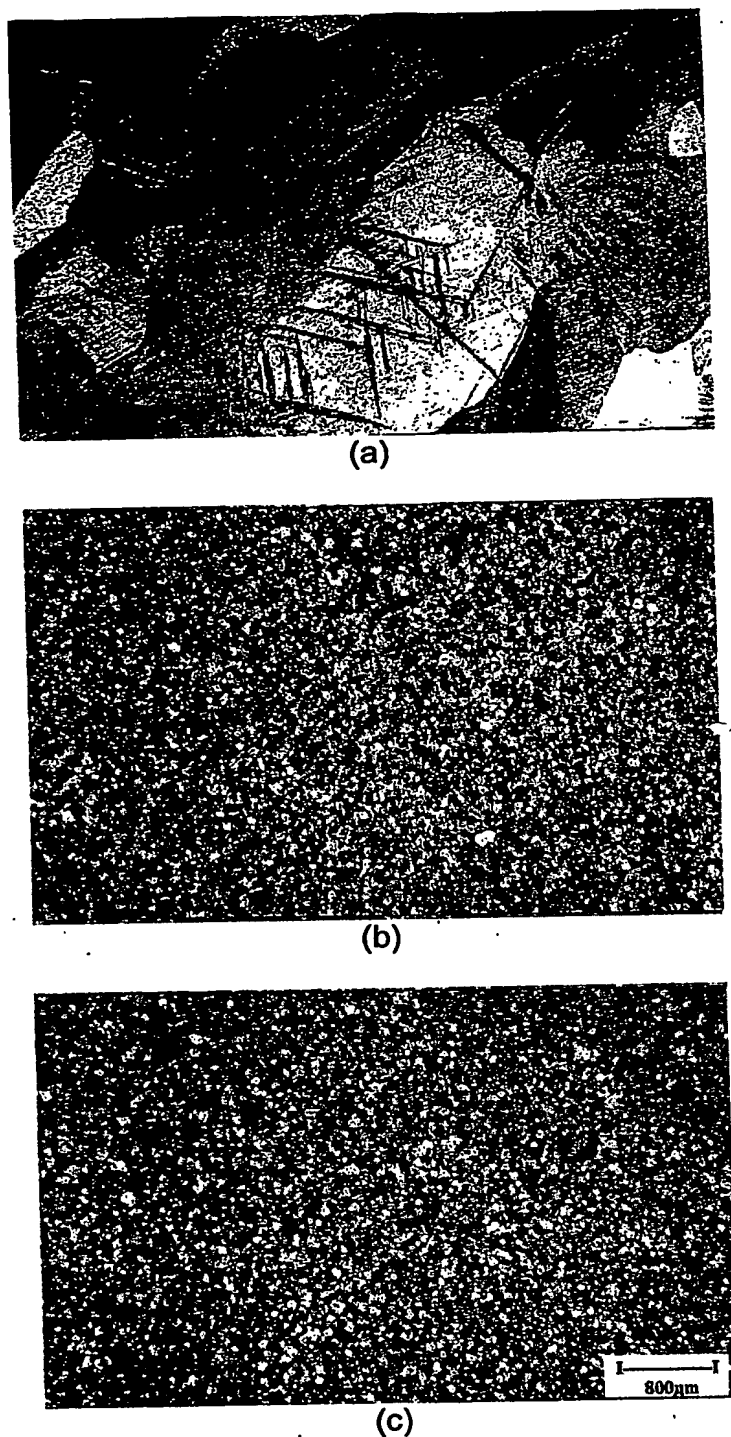
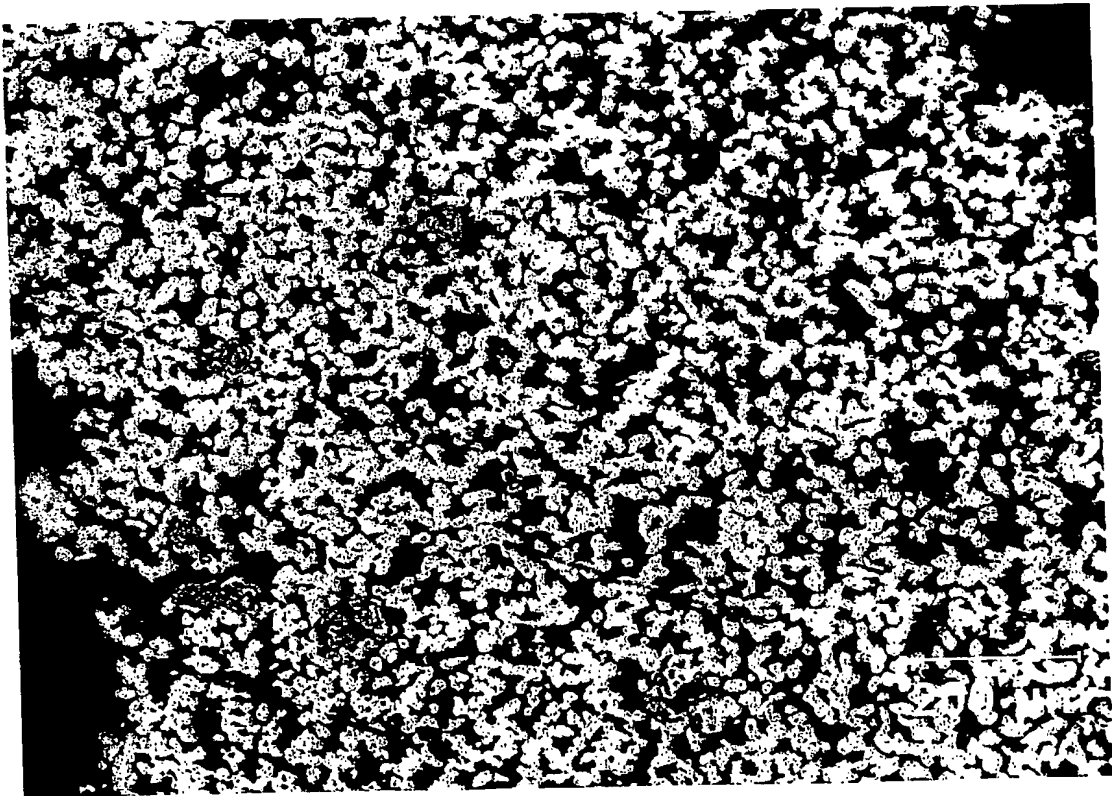


Figure 5 Optical micrographs showing the grain refining ability of pretreated sponge when added to pure magnesium at 800 °C. All micrographs are of the same magnification. (a) Pure magnesium, (b) after adding 1 wt% sponge, followed by 30 minutes manual stirring, and (c) after 30 minutes of holding following (b) and then restirring the melt for two minutes.

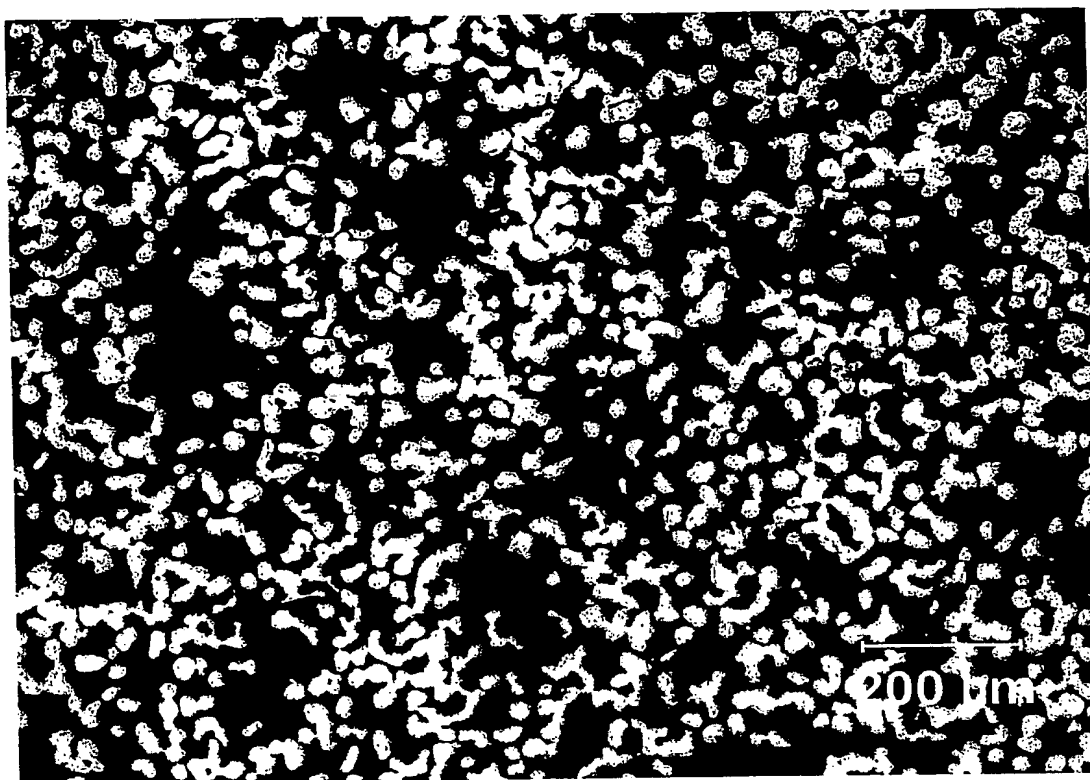


**Fig. 6**

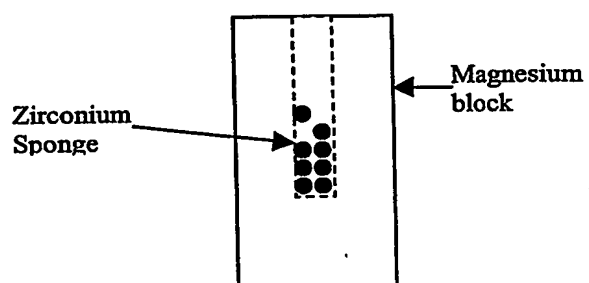


**Fig. 7**

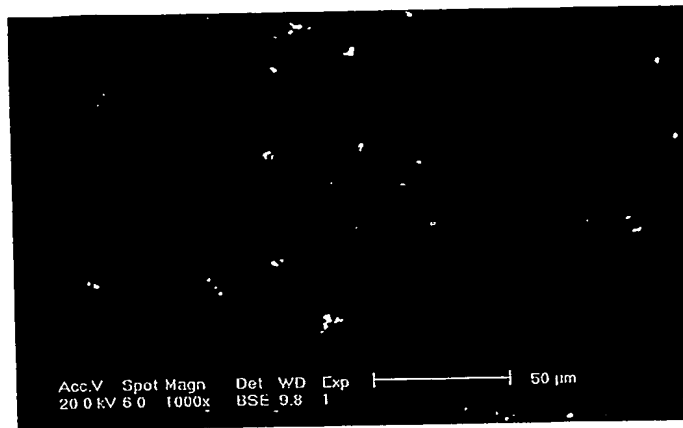




**Fig. 8**

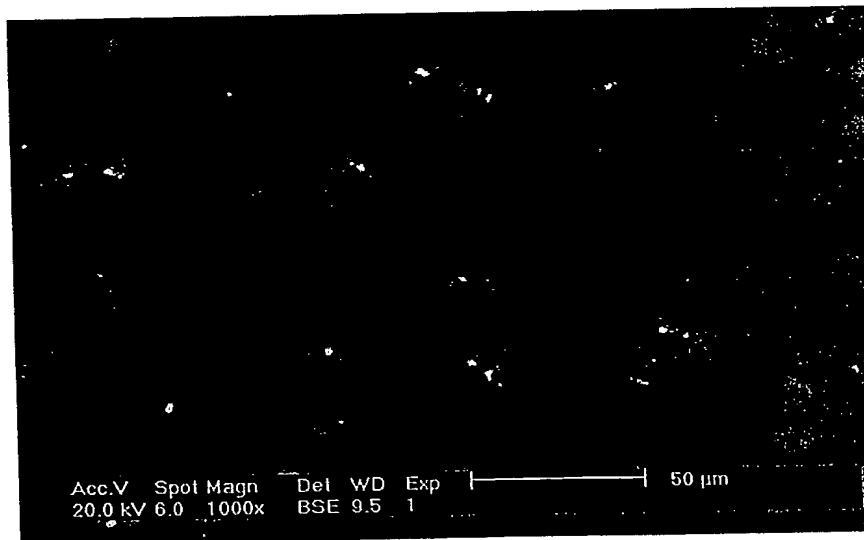


**Fig. 9**



A backscattered electron (BSE) image of the grain structures of one of the samples taken from the 730 °C alloying test, showing the white tiny zirconium particles and the zirconium-rich cores, further demonstrating that the use of zirconium sponge is comparable to that of Zirmax.

**Fig. 10**



A BSE image showing the zirconium-rich cores a sample alloyed with 1% zirconium addition in the form of the Zirmax master alloy.

**Fig. 11**

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